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Density, refraction index and vapor–liquid equilibria of N-methyl-2-hydroxyethylammonium butyrate plus (methyl acetate or ethyl acetate or propyl acetate) at several temperatures

V.H. Alvarez [a], S. Mattedi [b], M. Aznar [c,*]

[a] Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, AB, Canada T6G 2P5
[b] Chemical Engineering Department, Polytechnic School, Federal University of Bahia (UFBA), 40210-630 Salvador-BA, Brazil
[c] School of Chemical Engineering, State University of Campinas (UNICAMP), P.O. Box 6066, 13083-970 Campinas-SP, Brazil

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ABSTRACT

This paper reports the densities, refraction indices, and vapor liquid equilibria for binary systems ester + N-methyl-2-hydroxyethylammonium butyrate (m-2-HEAB): methyl acetate (1) + m-2-HEAB (2), ethyl acetate (1) + m-2-HEAB and propyl acetate (1) + m-2-HEAB (2). The excess molar volumes, deviations in the refraction index, apparent molar volumes, and thermal expansion coefficients for the binary systems were fitted to polynomial equations. The Peng–Robinson equation of state, coupled with the Wong–Sandler mixing rule, is used to describe the experimental data. Since the predictive activity coefficient model COSMO-SAC is used in the Wong–Sandler mixing rule, the resulting thermodynamic model is a completely predictive one. The prediction results for the density and for the vapor–liquid equilibria have a deviation lower than 1.0% and 1.1%, respectively.

1. Introduction

Actually, organic esters are important intermediates in chemical and pharmaceutical industries, and they are mostly produced by acid-catalyzed esterification reactions [1]. Various mineral acids have been used as catalysts for esterification, but they are extremely corrosive and need to be neutralized at the end of the reaction. Many acid-catalyzed organic reactions based on ionic liquids have been reported, among which esterifications are a hot topic [2]. Furthermore, at the end of the reaction, a direct liquid–liquid separation or distillation of the esters compounds from the reaction mixture appears very attractive in the case of derivatives that are volatile enough. Besides, the ionic liquid could be recycled after separation and purification stages.

By the accepted definition, room-temperature ionic liquids are salts that are liquids below 373 K, which are considered as potential substitutes to many traditional organic solvents in reaction and separation processes [3,4]. In spite of their importance and interest, accurate values for many of the fundamental physical–chemical properties of these compounds are either scarce or absent. In order to design any process involving ionic liquids in industrial scale, it is necessary to know several physical properties, including density and vapor–liquid equilibria in mixtures including ionic liquids. Since it is impossible to measure all the possible combinations of systems, it is necessary to make measurements on selective systems to provide results that can be used to develop correlations and predictive methods.

Most of the studies concerning ionic liquids have been based on the imidazolium cation and, to a lesser extent, on the alkyl pyridiniums and trialkylamines [5]. On the other hand, protic ionic liquids (PILs) have received limited attention from the academia, despite that the first PIL synthesized was the ethanolammonium nitrate, reported by Gabriel and Weiner in 1882 [6]. These PILs are produced by a stoichiometric acid–base Brønsted reaction and their main difference, compared to aprotic ionic liquids (AILs), is the presence of at least one proton, which is/are able to promote extensive hydrogen bonding [7]. Recently, some work has been reported on the synthesis, physicochemical and structural characterization of PILs. Bicak [8] synthesized the 2-hydroxyethylammonium formate (2-HEAF), an ionic liquid formed by the neutralization of monoethanolamine with formic acid. Greaves *et al.* [9] proposed different PILs from primary amines and organic and inorganic acids. Cota *et al.* [10], Kurnia *et al.* [11] and Alvarez *et al.* [12] synthesized several of these ionic liquids by modifying the aliphatic chain of the organic acid and/or using secondary and tertiary hydroxyamines. There were also studies that use PILs in catalytic reactions and on the interaction with hydroxilic

* Corresponding author. Tel.: +55 19 35213962; fax: +55 19 35213965.
E-mail address: maznar@feq.unicamp.br (M. Aznar).

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TABLE 1
Purity, water content by mass, w_{H2O}, and density, ρ, of pure components at $T = 298.15$ K and $p = 101.3$ kPa.

Compound	Source	Purification method	Mass fraction purity	Mass fraction w_{H2O} ($\times 10^2$)[a]	ρ (g · cm^{-3})	
					Exp	Lit
Methyl acetate	S-A[c]	None	>0.998[c]	<0.05	0.92682	0.9282[e]
Ethyl acetate	S-A[c]	None	>0.999[c]	<0.03	0.89490	0.8928[e]
Propyl acetate	S-A[c]	None	>0.995[c]	<0.5	0.88261	0.8823[e]
m-2-HEAB[b]	Synthesized	Vacuum heating	>0.980[d]	<0.1	1.03394	1.0392[f]

Standard uncertainties u are $u(\rho) = 0.00005$ g · cm^{-3} and $u(T) = 0.01$ K.
[a] Measured by Karl Fisher titration.
[b] m-2-HEAB = N-methyl-2-hydroxyethylammonium butyrate.
[c] Sigma–Aldrich.
[d] Measured by NMR method.
[e] Reference [16].
[f] Reference [12].

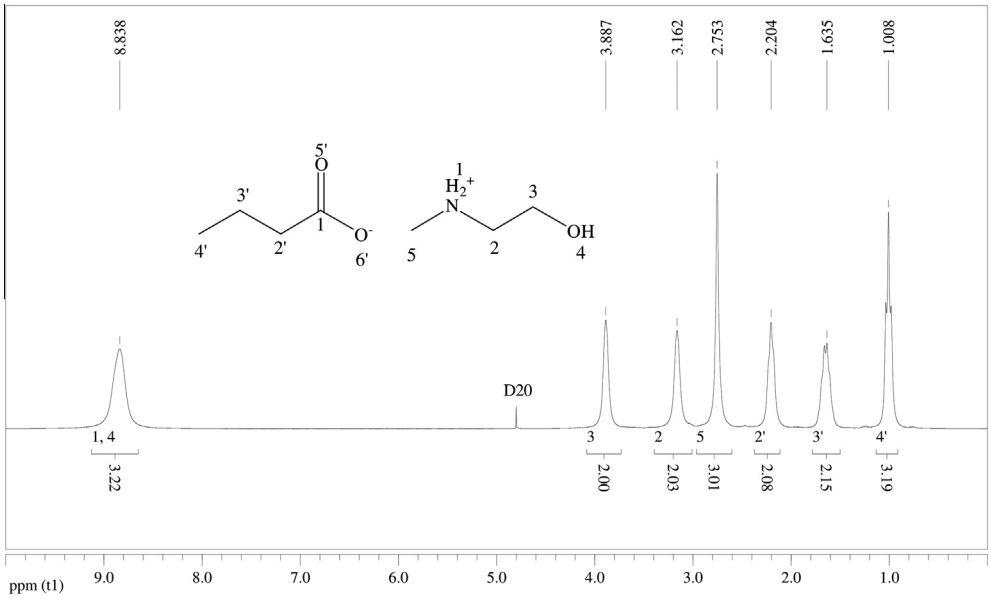

FIGURE 1. 1D hydrogen spectrum for m-2-HEAB.

solvents, showing that 2-HEAF is soluble in water, ethanol and methanol in all the concentration range [13]. Moreover, a relevant aspect, few times considered in the application of ionic liquids and the environment, is their potential toxicity. This issue has not been sufficiently studied, especially taking into account the need of this information to fulfill the REACH (Registration, Evaluation, Authorization and Restriction of Chemical Substances) requirements (UE) and so, allowing the assessment of hygiene and safety issues derived from their manufacture, use, and transport. Specifically about PILs from hydroxyamines and organic acids, the first results highlight that total biodegradation and low toxicity are intrinsic characteristics of this family of ionic liquids [14,15].

In this work, experimental density and refraction index data of pure protic ionic liquid N-methyl-2-hydroxyethylammonium butyrate (m-2-HEAB) have been measured at several temperatures. Also, experimental density, refraction index and vapor–liquid equilibrium (VLE) data over the whole composition range for binary mixtures methyl acetate (1) + m-2-HEAB (2), ethyl acetate (1) + m-2-HEAB (2) and propyl acetate (1) + m-2-HEAB (2) have been determined at 101.3 kPa. Thermal expansion coefficients, excess molar volumes, and deviations in the refraction index were calculated from experimental data. The Peng–Robinson equation of state, coupled with the Wong–Sandler mixing rule, was used to describe the experimental data. Since the predictive activity coefficient model COSMO-SAC was used in the Wong–Sandler mixing rule, the resulting thermodynamic model was a completely predictive one. The prediction results for the density and for the vapor–liquid equilibria had a deviation lower than 1.0% and 1.1%, respectively.

2. Experimental

2.1. Chemicals

The esters were supplied by Sigma–Aldrich, with purity higher than 99.0%, and were degassed ultrasonically.

2.2. Synthesis

N-methyl-2-hydroxyethylammonium butyrate was prepared according to the procedure by Alvarez *et al.* [12], slightly modified. Butanoic acid was added dropwise to a known amount of 2-(methylamino)ethanol and cooled in an ice bath under nitrogen in order to maintain the reaction temperature below 283.15 K, since the reaction is exothermic. The reaction mixture was stirred at room temperature for 5 h and the progress of the reaction was monitored by refraction index measurements. The ionic liquid N-methyl-2-hydroxyethylammonium butyrate obtained was dried